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Effects of feed solution characteristics and membrane fouling on N-nitrosamine rejection by reverse osmosis membranes

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Augmentation of potable water sources with reclaimed municipal wastewater is an option of increasing importance for water security in regions and countries where severe water stress occurs. Consequently, the presence of emerging trace contaminants in reclaimed water has been recognised as a critical issue due to their potential adverse health effects. Notable examples of these trace organic chemicals include N-nitrosodimethylamine (NDMA) and several other N-nitrosamines. Most of these N-nitrosamines have been classified by the US EPA as probable human carcinogens [1]. The Australian Guidelines for Water Recycling has established guideline values for these trace contaminants in the range from 1 to 10 ng/L [2]. Although reverse osmosis (RO) membrane filtration is frequently used in water reclamation application partly to ensure adequate removal of emerging trace contaminants, little is known about the rejection of N-nitrosamines by RO membranes. In fact, the reported rejection value of NDMA (even by the same RO membrane) varies widely from almost negligible level to 86% and the underlying reason for such significant variation in NDMA rejection remains unclear [3-6]. This study aims to delineate and reconcile the significant variation in the rejection of NDMA and other N-nitrosamines in the literature by investigating the effects of feed solution characteristics, operating conditions and membrane fouling on the rejection of eight N-nitrosamines by five different NF/RO membranes. Membrane fouling was simulated using real tertiary treated effluent and model foulants. This study appears to be the first of its kind, in which the rejection of all eight relevant N-nitrosamines by NF/RO membrane was systematically investigated.

A bench-scale cross flow membrane filtration system was used in this study. Unless otherwise stated, in all experiments, N-nitrosamines were spiked into the feed solution at environmentally relevant concentration (i.e. 250 ng/L) and the permeate flux was set at 20 L/m^2h which is a typical value for water reclamation RO plants. Results obtained from this study indicate that the rejection of N-nitrosamines by NF/RO membrane is governed mostly by steric hindrance (Figure 1). N-nitrosamine rejection increased in the increasing order of their molecular weight and decreasing order of desalting capacity (or NaCl rejection) of the membrane (Figure 1). The impact of membrane type on rejection of N-nitrosamines was less pronounced for the higher molecular weight compounds. Results reported in Figure 1 also suggest that membrane selection is important to ensure adequate rejection of the low molecular weight N-nitrosamines, particularly NDMA. The results reported here are in good agreement with several previous studies in which a subset of these N-nitrosamines were investigated [7-8].

The impacts of feed solution characteristics were also investigated using the clean water matrix. Changes in the feed concentration in the range from 250 – 1,500 ng/L did not cause any discernible influence on their rejection. On the other hand, changes in the permeate flux from 5 to 60 L/m^2h resulted in an increase in NDMA and NMEA rejection (from 25 to 63% and from 49 to 89%, respectively). The impact of permeate flux on rejection of other N-nitrosamines with higher molecular weight was less pronounced. Amongst the eight N-nitrosamines investigated here, NDMA rejection was most affected by feed solution characteristics. For example, a ten-fold increase in ionic strength in the feed (from 26 to 260 mM) led to a discernible decrease in NDMA rejection (from 52 to 34%). In addition, an increase in the feed solution pH (i.e. from 6 to 8) resulted in a small but clearly discernible increase in the rejection of NDMA (from 33 to 37%). Most importantly, an increase in the feed temperature caused a considerable decrease in the rejection of all N-nitrosamines. For example, when the feed temperature increased from 20 to 30°C, the rejection of NDMA, NMEA and NPYR decreased from 49 to 24%, 81 to 62%, and 90 to 74%, respectively (Figure 2). The results indicate that permeate flux, pH, ionic strength, and

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temperature of the feed solution can affect the rejection of NDMA and in some cases other N-nitrosamines.

Fouling with tertiary effluent generally caused an increase in N-nitrosamine rejection (Figure 3). This is particularly apparent for low molecular weight N-nitrosamines such as NDMA. Membrane fouling by tertiary effluent led to an increase in NDMA rejection from 11 to 34% by the NF90 membrane and from 34 to 73% by the ESPA2 membrane. The impact of membrane fouling was less pronounced for a high rejection RO membrane (ESPAB). Membrane fouling on the ESPAB membrane caused only a slight increase in NDMA rejection in the range from 82 to 88%. The observations also suggest that the ESPAB membrane is very effective to reject N-nitrosamines regardless membrane fouling. To understand the mechanism of fouling impact on N-nitrosamine rejection, further experiments were conducted using three model foulants. Sodium alginate, humic acid and colloidal silica (Ludox CX) were selected as model foulant to simulate polysaccharides, refractory organic matter and colloidal particles, respectively. Interestingly, membrane fouling with these model foulants had only negligible impacts on the rejection of N-nitrosamines (data not shown). In general, the molecular size of these model foulants is larger than those in tertiary effluent. The improvement in N-nitrosamine rejection with tertiary effluent fouling thus might be explained by a dense fouling layer which hinders the transport of N-nitrosamines across the membrane.

The results reported here suggest that the combined effects of these feed solution characteristics and membrane fouling may account for some of the variation of NDMA rejection by RO membranes previously reported in the literature. In particular, the findings regarding feed temperature need to be interpreted with caution because temperature variation in the range from 20 to 30°C is likely to occur at many water reclamation plants employing RO membranes and is usually difficult to control. It is also important to note that the rejection of N-nitrosamines is likely to vary widely due to membrane fouling during long-term operation. The present findings might help to predict variations in NDMA rejection during water reclamation plant operation.

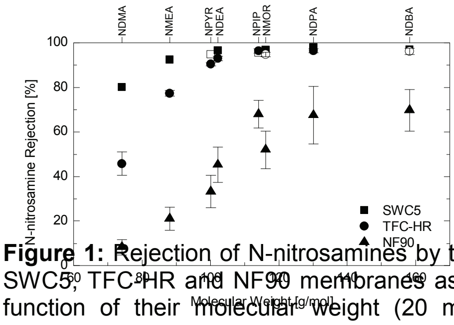

Figure 1: Rejection of N-nitrosamines by the SWC5, TFC-HR and NF90 membranes as a function of their molecular weight (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, permeate flux 20 L/m^2h, cross flow velocity 40.2 cm/s, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1ºC). Open symbol (□ and ○) indicates that the permeate concentration was below the instrumental detection limit. Error bars show the standard deviation of three replicate experiments.

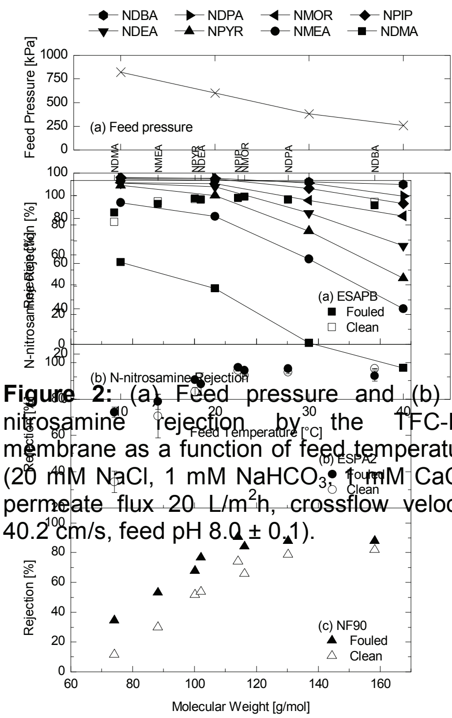

Figure 2: (a) Feed pressure and (b) N-nitrosamine rejection by the TFC-HR membrane as a function of feed temperature (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, permeate flux 20 L/m^2h, crossflow velocity 40.2 cm/s, feed pH 8.0 ± 0.1).

Figure 3: Effects of membrane fouling using tertiary effluent on the rejection of N-nitrosamines (a) ESPAB, (b) ESPA2 and (c) NF90 membranes. Experimental conditions are as caption of Figure 1. Error bars on the ESPA2 membrane show the standard deviation of two replicate experiments.

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